“Batteries 101”
overview of battery technologies, markets, and recycling

Robert Spotnitz, President, Battery Design LLC

Public Workshop on Lead-acid Batteries and Alternatives

9:30 – 10:00 am Monday, November 6, 2017

CalEPA Headquarters, Pacific Time Klamath Room

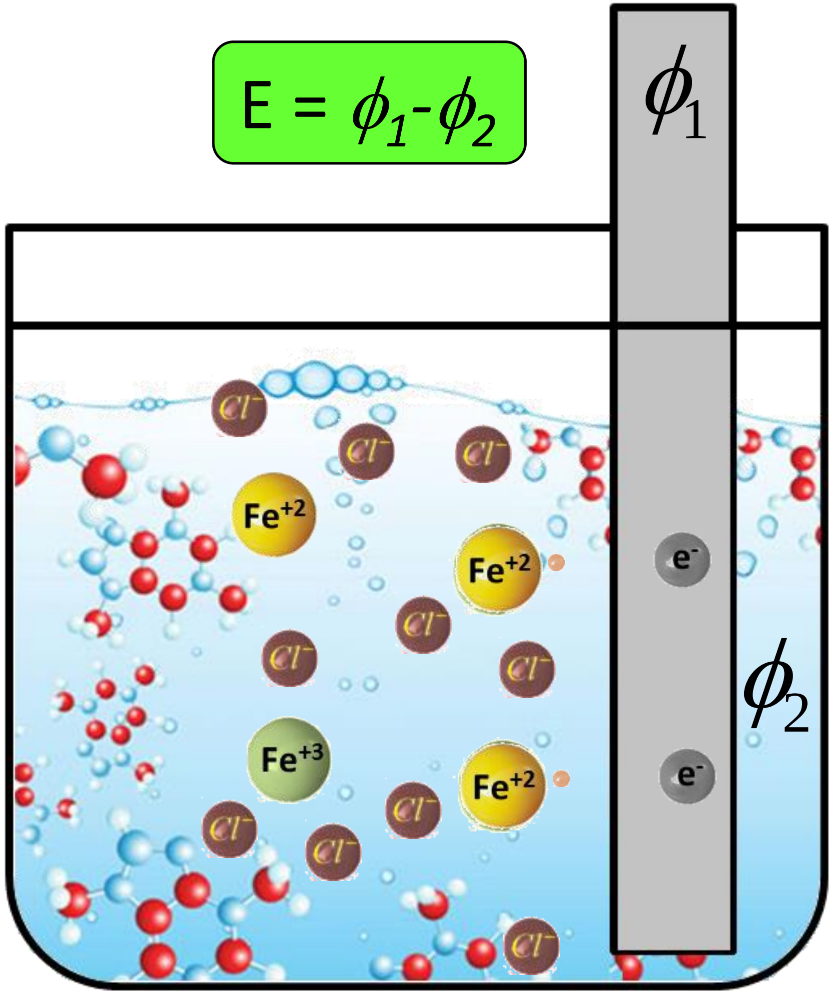
1001 I Street, Sacramento, CA 95814

Electrode		Electrode reaction	E^0/V
Au	Gold	$Au^{3+} + 3e^- \rightleftharpoons Au$	+1.43
Ag	Silver	$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
Cu	Copper	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
H	Hydrogen	$H^+ + e^- \rightleftharpoons H$	0
Pb	Lead	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0.13
Sn	Tin	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0.14
Ni	Nickel	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0.25
Cd	Cadmium	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	−0.40
Fe	Iron	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.44
Zn	Zinc	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76
Ti	Titanium	$Ti^{2+} + 2e^- \rightleftharpoons Ti$	−1.63
Al	Aluminium	$Al^{3+} + 3e^- \rightleftharpoons Al$	−1.66
Mg	Magnesium	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.37
Na	Sodium	$Na^+ + e^- \rightleftharpoons Na$	−2.71
K	Potassium	$K^+ + e^- \rightleftharpoons K$	−2.93
Li	Lithium	$Li^+ + e^- \rightleftharpoons Li$	−3.05

Electrochemical Series

http://www.glogster.com/nanospecs/electrochemical-series/g-6lkta0gu7ju9lo54qu4q8a0

Electrochemistry



i_0 exchange current density

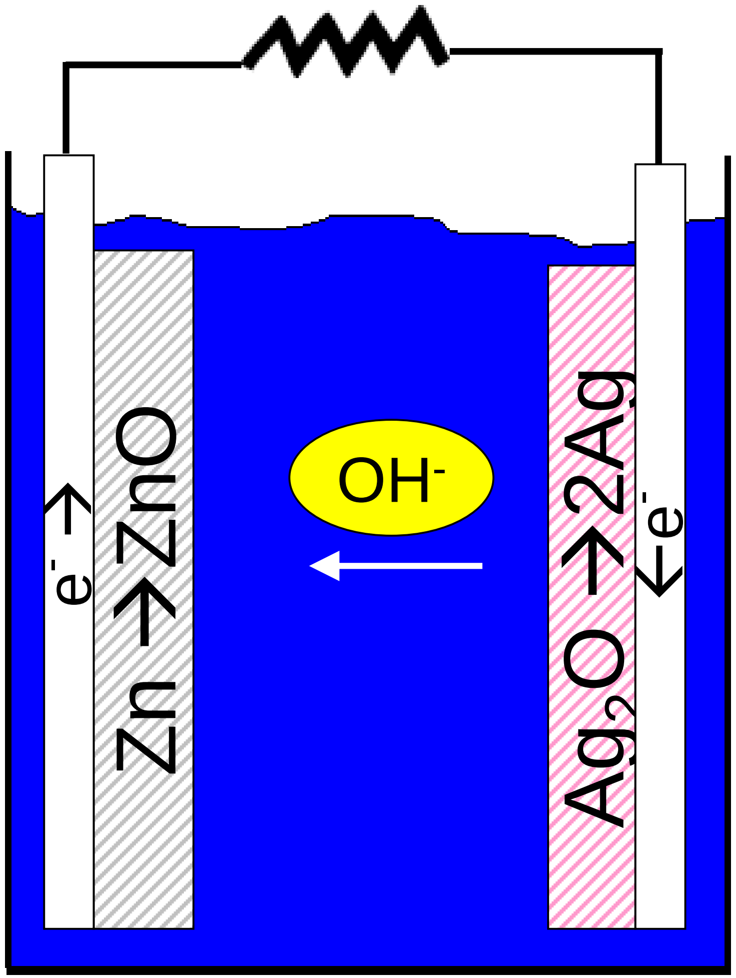
What is a battery?

- A battery or "galvanic cell" converts chemical energy to electrochemical energy using ***at least one of reactant stored in a cell*.**
- A fuel cell converts chemical energy to electrochemical energy using reactants stored externally.
- A capacitor stores and releases electrical energy using double-layer charge separation or a pseudo-capacitive effect such as surface adsorption, reaction or bulk intercalation.

Volta's pile
Ag/Zn (1800)

March 1800, *"... In this manner I continue coupling a plate of silver with one of zinc, and always in the same order, that is to say, the silver below and the zinc above it, or vice versa, according as I have begun,* ***and interpose between each of those couples a moistened disk****. "*.

Terminology

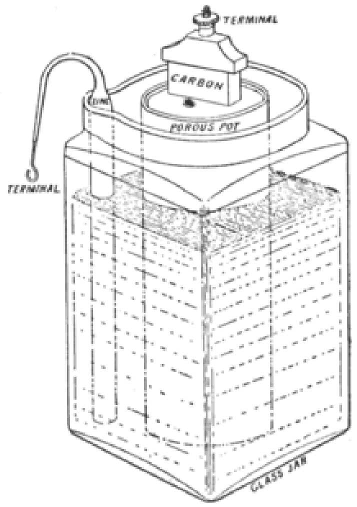


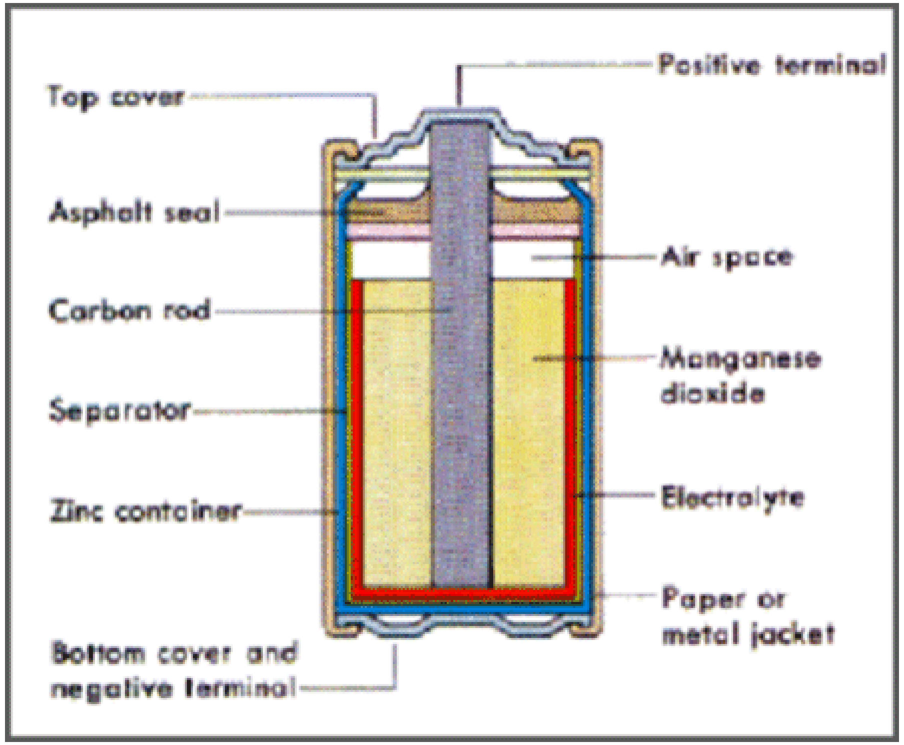
- Battery consists of one or more cells
- Cell consists of a pair of electrodes and an ion conductor
- Electrode consists of active material, current collector, and tab
- Positive electrode is called "cathode"
- Negative electrode is called "anode"
- Package, separator, insulators, etc.

Leclanché Cell – primary cell

In 1866, Georges Leclanché invented a battery that consisted of a zinc anode and a manganese dioxide cathode wrapped in a porous material, dipped in a jar of ammonium chloride solution. The manganese dioxide cathode had a little carbon mixed into it as well, which improved conductivity and absorption.[7] It provided a voltage of 1.4 volts.[8] This cell achieved very quick success in telegraphy, signaling and electric bell work.

https://en.wikipedia.org/wiki/History_of_the_battery





http://www.telephonecollecting.org/leclanche.html

The use of porous electrode provides power and energy.

Alkaline Chemistry

Dry cell invented in 1866 by G. Leclanché (1839-1882).

Invented in 1959 by Lew Urry (1927-2004) at Union Carbide.

$$MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^-$$

$$3MnOOH + e^- \rightarrow Mn_3O_4 + OH^- + H_2O$$

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^- \quad (II)$$

$$Zn + 4OH^- \rightarrow Zn(OH)_4^{-2} + 2e^- \quad (III)$$

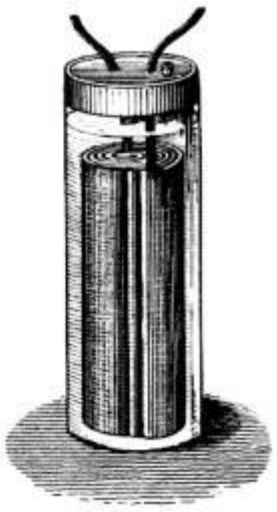
Zincate can migrate into separator and precipitate.

Lead-Acid Battery

In 1859, Gaston Planté invented the lead–acid battery, the first-ever battery that could be recharged by passing a reverse current through it. A lead acid cell consists of a lead anode and a lead dioxide cathode immersed in sulphuric acid.

Planté's first model consisted of two lead sheets separated by rubber strips and rolled into a spiral.[6] His batteries were first used to power the lights in train carriages while stopped at a station.

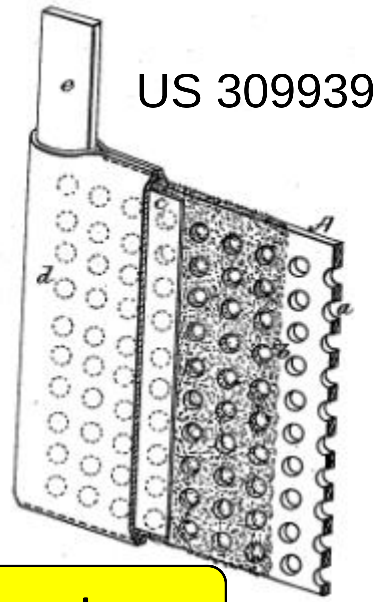
https://en.wikipedia.org/wiki/History_of_the_battery



In 1880, Faure patented a method of coating lead plates with a paste of lead oxides, sulphuric acid and water, which was then cured by being gently warmed in a humid atmosphere. The curing process caused the paste to change to a mixture of lead sulphates which adhered to the lead plate. During charging the cured paste was converted into electrochemically active material (the "active mass") and gave a substantial increase in capacity compared with Planté's battery.[5] This was a significant breakthrough that led to the industrial manufacture of lead-acid batteries, as now used for starting motor cars.

https://en.wikipedia.org/wiki/Camille_Alphonse_Faure

Fig. 1.

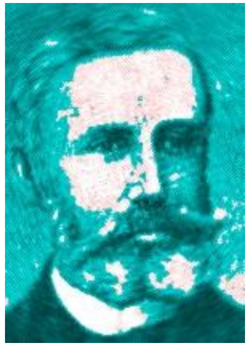


US 309939 A

The porous electrode is one of the most important innovations in battery technology.

Lead-Acid Batteries

- 1859, invented by Gaston Planté
- Key characteristics
  - low-cost
  - must be stored at full state of charge
  - best for shallow discharge cycles
  - poor high-rate charge acceptance
  - good low-temperature performance
  - high voltage (~2 V)



1834-1899

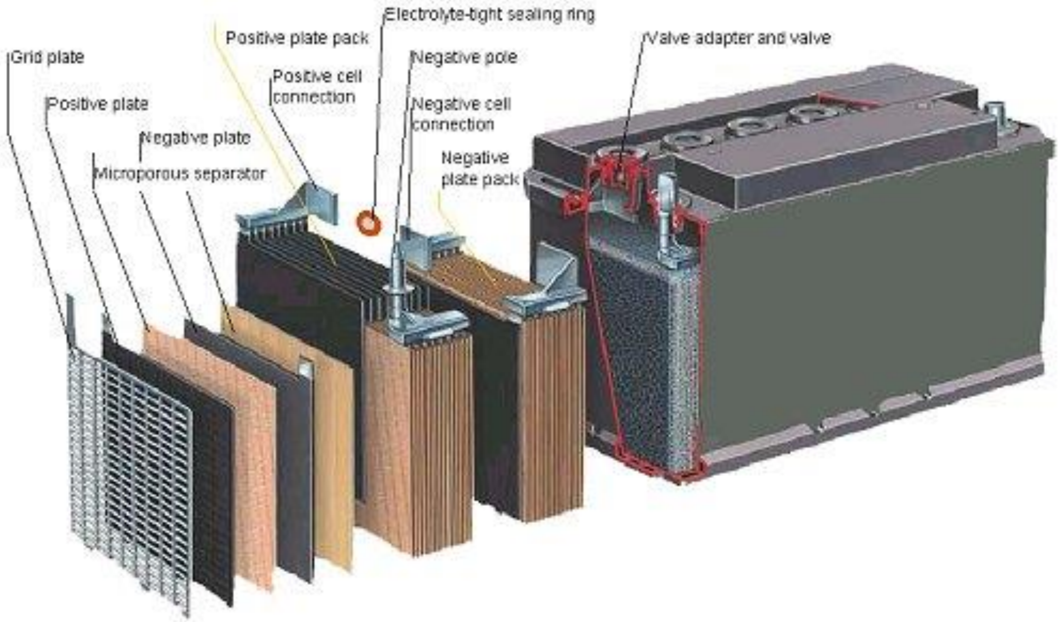
Major innovation: Gas recombination (1947)
- Flooded
- Valve Regulated Lead Acid (VRLA) or SLA

Major application: car battery for Starting Lighting Ignition (SLI)

$$2Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 4H^+ + 4e^-$$

$$PbO_2 + 4e^- + 2H_2SO_4 \rightarrow PbSO_4 + 2H_2O + 2SO_4^{2-}$$

$$PbO_2 + 2Pb + 3H_2SO_4 \rightarrow 3PbSO_4 + 2H_2O$$

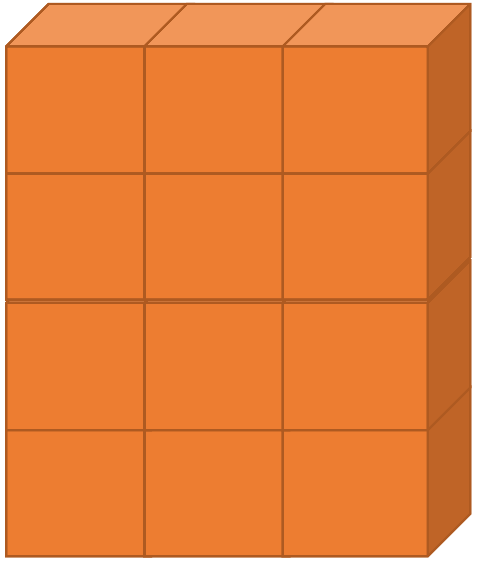


http://www.lead-battery-recycling.com/the-history-of-battery.html

Intercalation Battery

Negative "hotel"

Positive "hotel"



Stable structures
$\rightarrow$Long calendar life

Gentle, reversible process
$\rightarrow$ Long cycle life

Metal hydrides – (1967?)

$Li_4Ti_5O_{12}$ – Murphy (1983)
Carbons – Yoshino (1986)

NiOOH/Ni$(OH)_2$ – Jungner (1899)

TiS_2 – Whittingham (1975)
$LiCoO_2$ – Goodenough (1980)
LiMn2O4 – Thackeray/Goodenough (1983)
$LiFePO_4$ – Goodenough (1999)
$LiNiMnCoO_2$ – Thackeray (2001)

The lithium-ion intercalation battery is becoming the dominant battery technology.

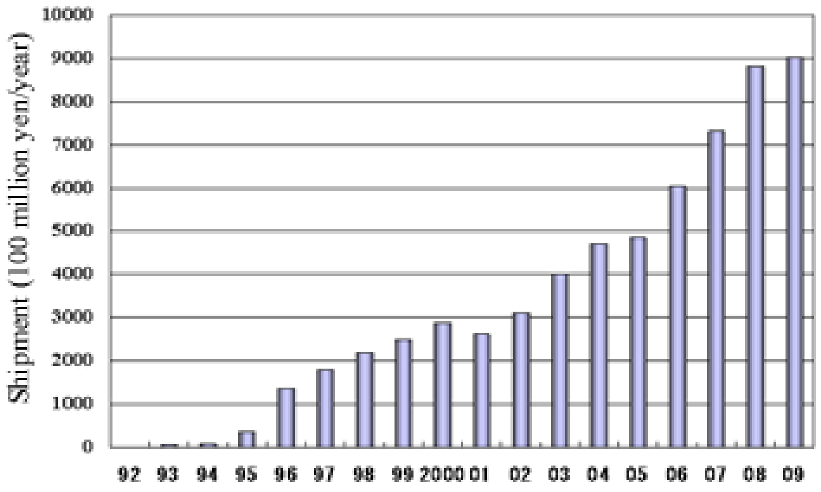
Li-Ion Batteries

- Invented in 1985 by Akira Yoshino (Asahi Kasei Corp.)
- Commercially introduced in 1991 (Sony)
- Key advantages
  - Long cycle life
  - Good calendar life
  - Good Wh/kg, Wh/liter
  - High discharge rate
  - High voltage ~3.7 average
  - Low self discharge

$$LiC_6 \Leftrightarrow C_6 + Li^+ + e^-$$

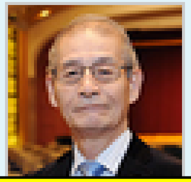
$$Li^+ + e^- + 2Li_{0.5}CoO_2 \Leftrightarrow 2LiCoO_2$$

$$LiC_6 + 2Li_{0.5}CoO_2 \Leftrightarrow 2LiCoO_2 + C_6$$



http://www.mst.or.jp/prize/english/winners/material/material2011_en.html

Robotics
Grid storage
Electric vehicles
Industrial (forklifts, etc.)
Tablets
Cellphones
Laptops
Camcorders

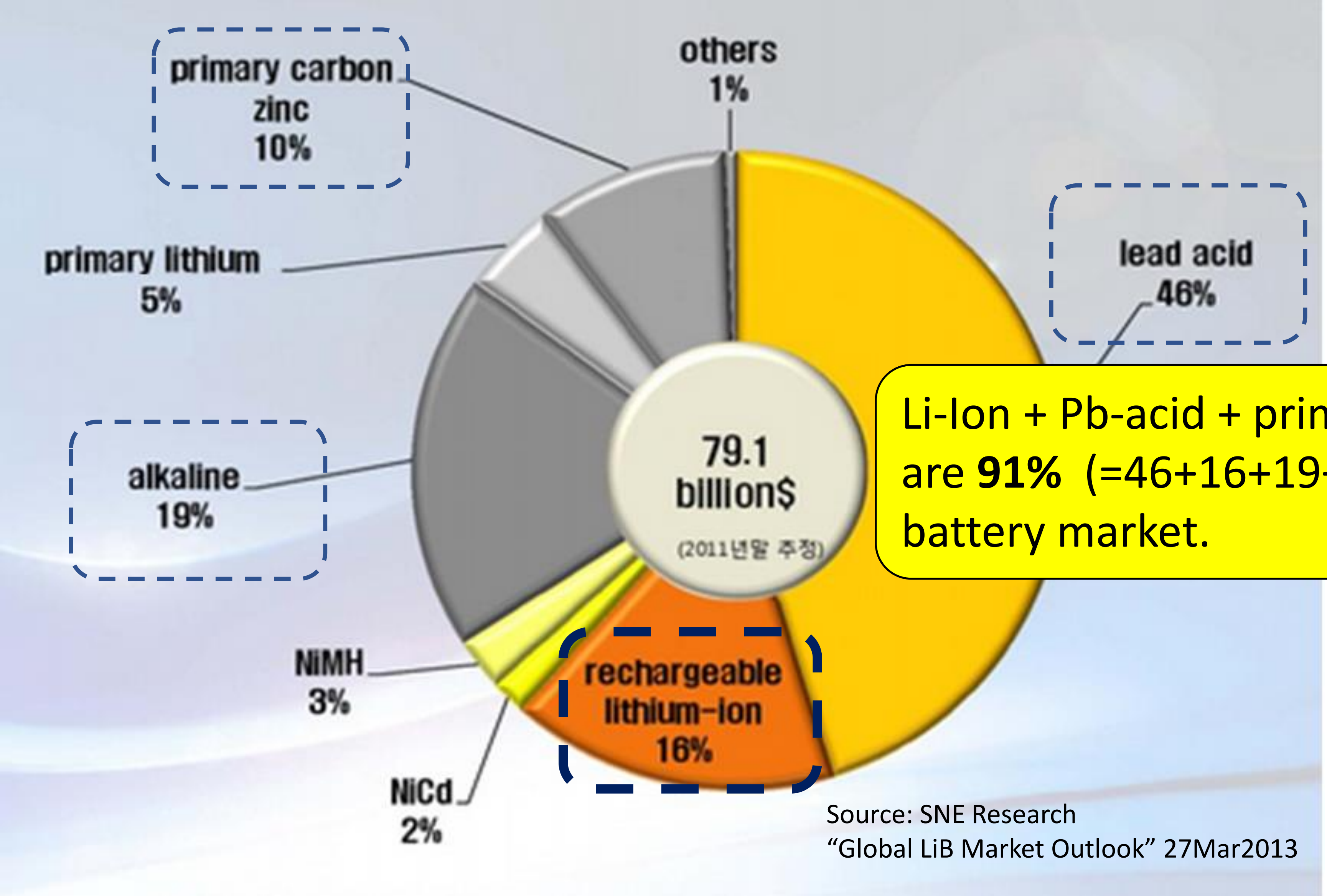


Dr. Akira Yoshino
General Manager, Yoshino Laboratory
Asahi Kasei Corporation

Award: Draper
Year: 2014
Citation: For engineering the rechargeable lithium-ion battery that enables compact, lightweight mobile devices.

Downsides are safety (flammability of organic electrolyte, overcharge and internal short circuit) and cost.

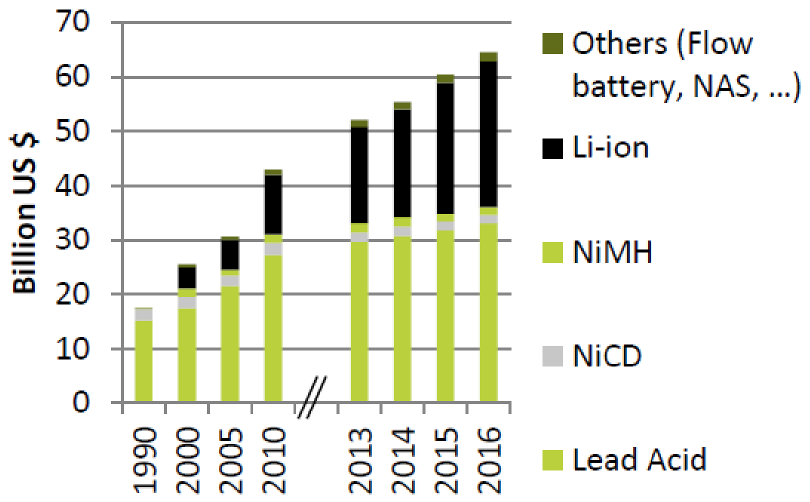
Global Battery Market

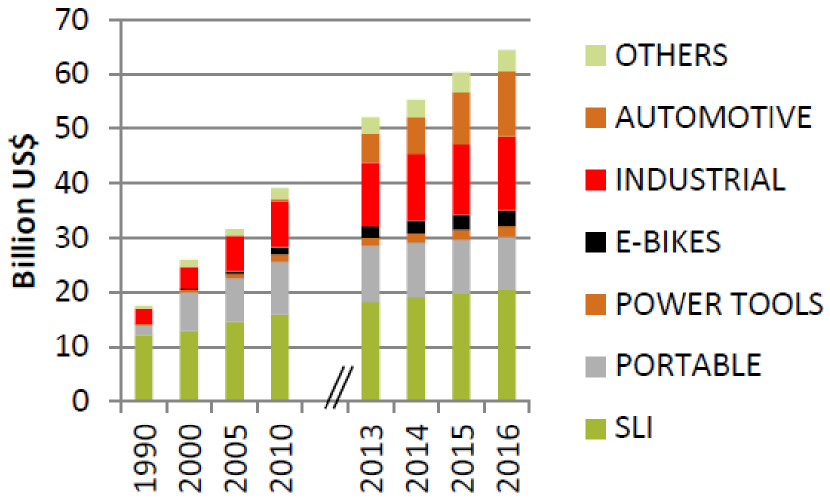


Li-Ion + Pb-acid + primary MnO_2/Zn are **91%** (=46+16+19+10) of battery market.

Source: SNE Research
“Global LiB Market Outlook” 27Mar2013

Worldwide Rechargeable Battery Market 1990-2016 5% average growth per year





SLI: Start light and ignition batteries for cars, truck, moto, boat etc...

PORTABLE: concumer electronics (cellular, portable PCs, tablests, Camera, ...), data collection & handy terminals,

POWER Tools: power tools but also gardening tools

1- Pack: cell, cell assembly, BMS, connectors – Power electronics (DC DC converters, invertors...) not included

Source: AVICENNE ENERGY, 2017

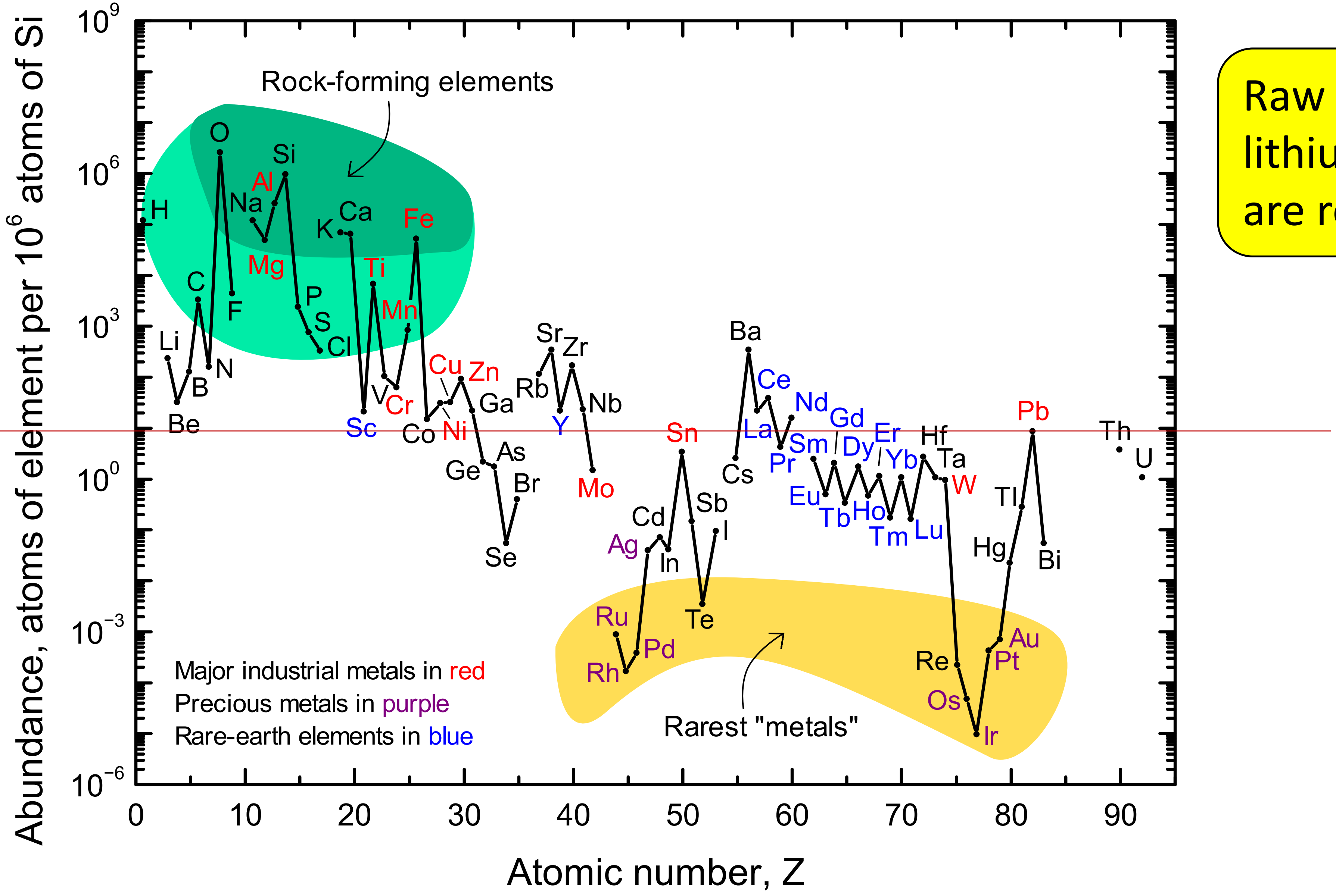
INDUSTRIAL
- MOTIVE: Forklift (95%), others
- STATIONARY: Telecom, UPS, Energy Storage System, Medical, Others (Emergency Lighting, Security, Railroad Signaling,, Diesel Generator Starting, Control & Switchgear,

AUTOMOTIVE: HEV, P-HEV, EV

OTHERS: Medical: wheelchairs, medical carts, medical devices (surgical power tools, mobile instrumentation (x-ray, ultrasound, EKG/ECG, large oxygen concentrators

Pb-acid is largest market ($) for rechargeable batteries
Lithium-ion is fastest growing chemistry.

Abundance of Elements in Earth's Crust



Raw materials for lithium-ion batteries are relatively plentiful

https://upload.wikimedia.org/wikipedia/commons/0/09/Elemental_abundances.svg

Typical properties of major battery chemistries

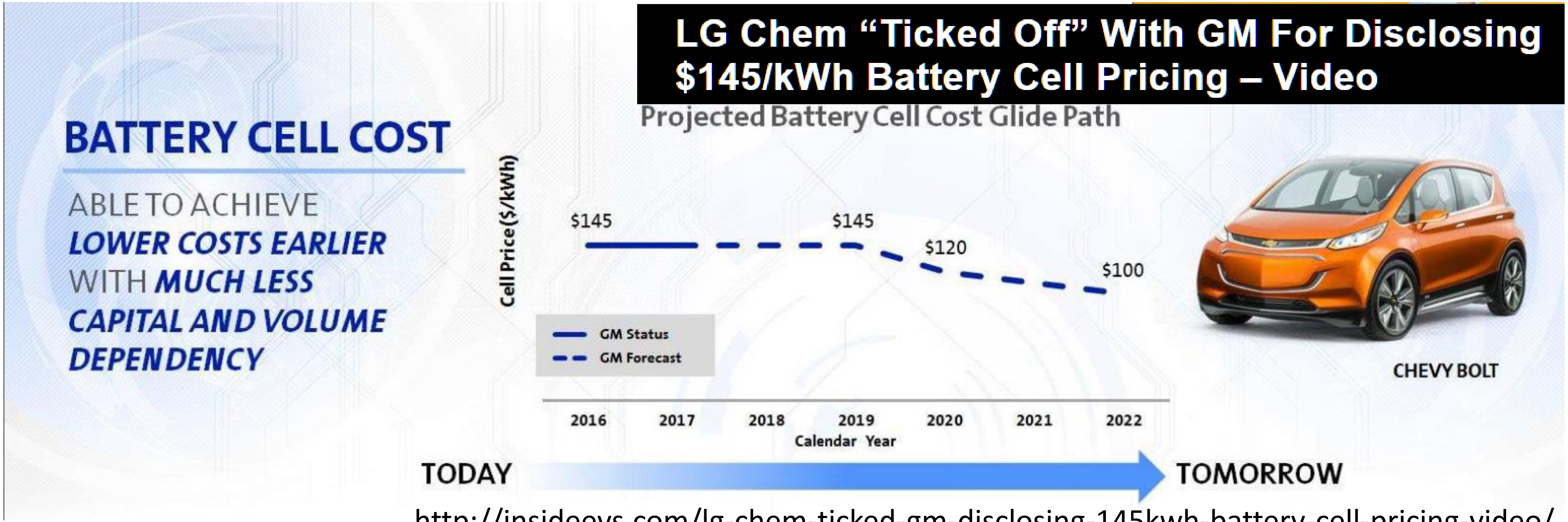
Type	Chemistry	Size mm	Typical Values: Capacity Ah	% Capacity retained after 6 months	Specific Energy Wh/kg	Energy Density Wh/l	Discharge time h	Retail Price $	Use	Retail Price, $/Wh
Primary	Alkaline	AA (14.5 dia x 50.5 tall)	2.85	100%	145	410	50	0.8	Toys	0.13
	Zinc-Air	Button (7.8 dia x 3.6 tall)	0.13	100%	360	1110	300	0.5	Hearing aid	2.56
	Li/MnO2	2/3 A (17 dia x 27 tall)	1.3	100%	200	315	1	5	Camera	1.28
Secondary	Pb acid	273 x 173 x 229	44	50%	29	52	6	68	Car	0.12
	Ni/Cd	AA	1	70%	40	120	0.1	2.5	Power tool	0.23
	Ni/MH	AA	1.7	80% (3 months)	67	220	1	2.8	Camcorder	0.56
	Li-Ion	18650 (18 dia x 65 tall)	1.8	>90%	100-250	330-750	2	2.5	Cellphone	0.27

Li-ion is superior to Alkaline and Pb acid on nearly every metric except price.

Audi claims to be buying batteries at ~$114/kWh for its upcoming electric cars, says CTO

Fred Lambert - Jun. 28th 2017 12:14 pm ET @FredericLambert

https://electrek.co/2017/06/28/audi-electric-car-battery-cost/



http://insideevs.com/lg-chem-ticked-gm-disclosing-145kwh-battery-cell-pricing-video/

ElectronicDesign. Feb 23, 2017

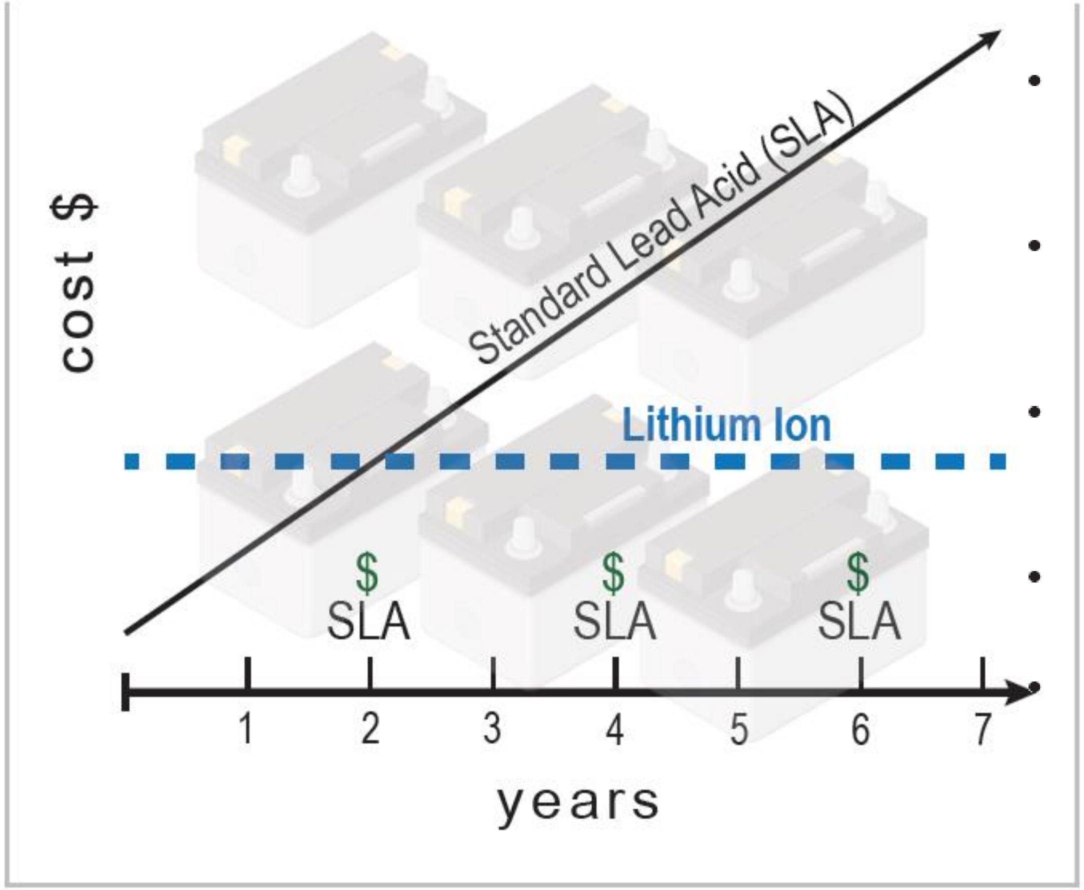
Lead-Acid Battery Applications Drive the Li-ion Market

Although important, neither consumer electronics nor electric vehicles are the main forces behind the growth in new battery technologies—instead it's coming from "everything else."

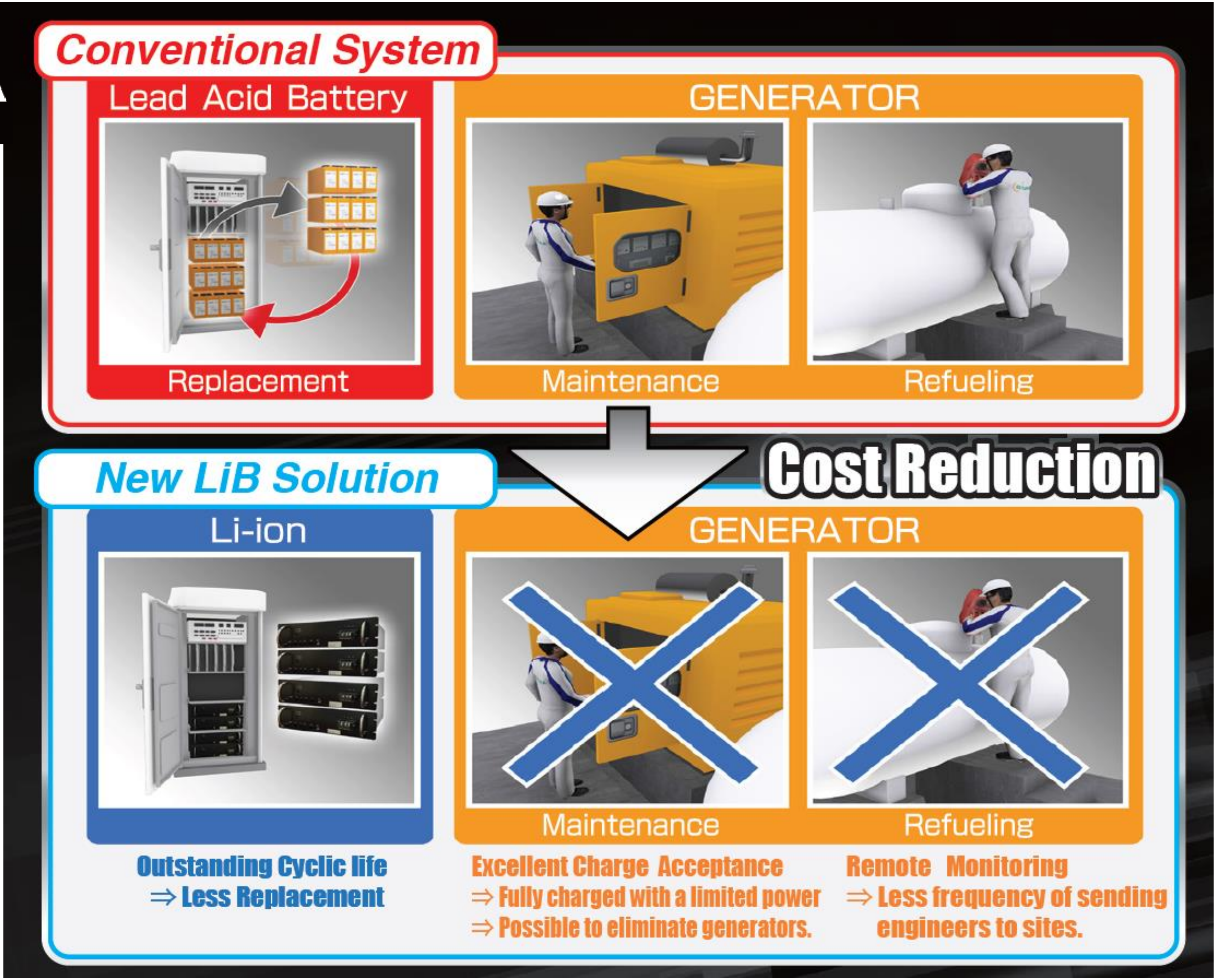
Sealed Lead Acid (SLA)

- SLA is simple, dependable, robust, and inexpensive, and can be used in a wide range of temperature environments.
- The batteries must be stored full state-of-charge (SOC), and they don't lend themselves to fast charging.
- The flip side to the charge constraints is that SLA batteries can use simple float or trickle chargers.
- SLA batteries are very heavy; their gravimetric energy density is very low.
- Cycle life is usually 200 to 300 cycles, but even a "deep cycle" SLA is damaged by repeated full discharges, causing cycle lifeto be as low as 50 cycles.
- The sloped discharge curve enables SOC measurement with simple voltage monitoring

Sealed lead-acid U1 battery	VS.	Lithium-iron-phosphate U1 battery
1.5 hrs	**Run time** (based on chemistry energy density at 175-W load)	2 hrs
60%	**Shelf life** (after 12 months with % nominal capacity at 68°F/20°C)	100%
250 cycles	**Cycle life** (100% DoD to 80%)	2000 cycles
28 lbs	**Weight** (comparing one 40-Ah battery)	10.4 lbs
< 1 year	**Lifespan** (based on daily use)	5+ years
$750	**Total cost of ownership** (based on 5-year span)	$450



- Lighter & Smaller - More portability
  - Half the weight of SLA
  - Half the volume of SLA
  - 2x energy density per unit weight
- Longer Shelf Life
  - Replacement every 5-7 year vs. 18 months - 2 years with SLA
- Temperature Range
  - No degredation at high temperatures
  - No air conditioning required
- Efficiency
  - Faster recharge time
  - 20-25% higher turnaround charge efficiency
- Cycling
  - More discharge cycles (5-10x)
  - Full depth of discharge capability vs. only 50% for SLA
- State of Charge & Remote Monitoring
  - Can be easily & remotely monitored
- Service
  - No servicing or watering required
  - No need for hydrogen gas extraction provisions


Conventional System
Lead Acid Battery
Replacement
GENERATOR
Maintenance
Refueling
Cost Reduction
New LiB Solution
Li-ion
GENERATOR
Maintenance
Refueling
Outstanding Cyclic life
⇒ Less Replacement
Excellent Charge Acceptance
⇒ Fully charged with a limited power
⇒ Possible to eliminate generators.
Remote Monitoring
⇒ Less frequency of sending engineers to sites.

Waste Prevention Information Exchange

Batteries

Also see Fluorescent Lamps and Tubes and Universal Waste.

All batteries are considered hazardous waste in California when they are discarded. This includes all batteries of sizes AAA, AA, C, D, button cell, 9 Volt, and all other batteries, both rechargeable and single use. **All batteries must be** recycled, or taken to a household hazardous waste disposal facility, a universal waste handler (e.g., storage facility or broker), or an authorized recycling facility.

What are the issues with battery recycling?

Posted by Cindy Miller on Tue, Nov 25, 2014 7:30:00 AM

Batteries, like many other types of electronic waste, contain harmful chemicals that can wreak havoc on the environment as well as being hazardous to people. A variety of materials are used to make batteries, some more dangerous than others.

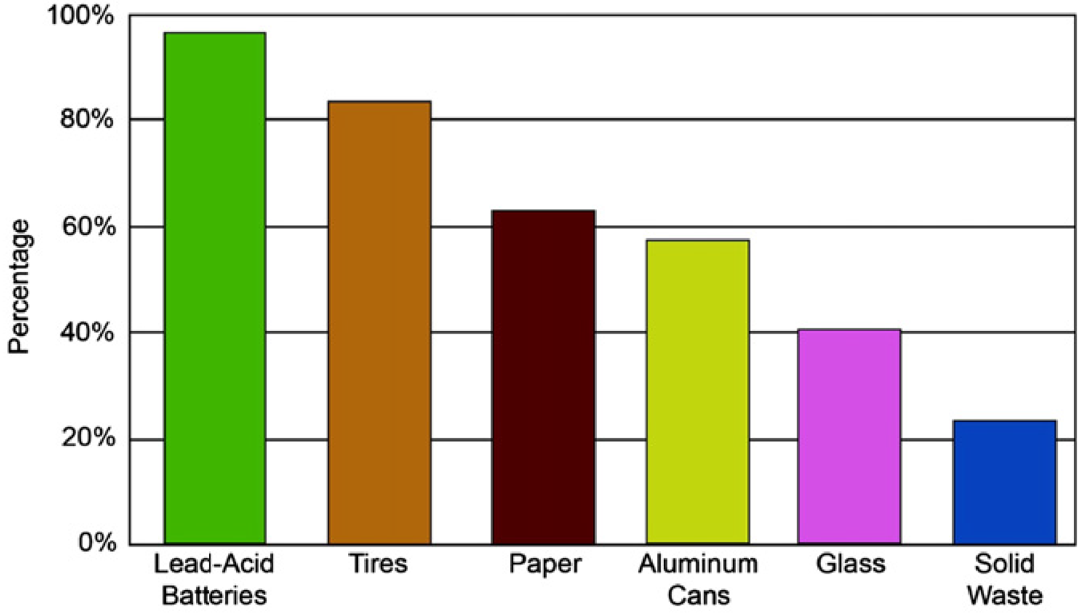
Lithium-ion (Li-ion) is the fastest growing type of battery, and is often found in notebook computers and mobile phones. Nickel-cadmium (Ni-cad) batteries have been used heavily in photography equipment and portable electronics. Lead-acid batteries are typically reserved for car batteries because of their large power-to-weight ratio and low cost.

Alkaline batteries are the single-use AA, AAA, and C batteries often utilized in household electronics. Alkaline batteries account for 80% of manufactured batteries in the US and over 10 billion individual units produced worldwide. An important difference between these single-use alkaline batteries and the majority of other types of e-waste is that these batteries are not rechargeable and are rarely recycled, so they often end up in a landfill.

Unlike single-use batteries, rechargeable batteries typically have a very high rate of recycling. Most rechargeable batteries are recycled along with the device that contained them at the end of their usable life.

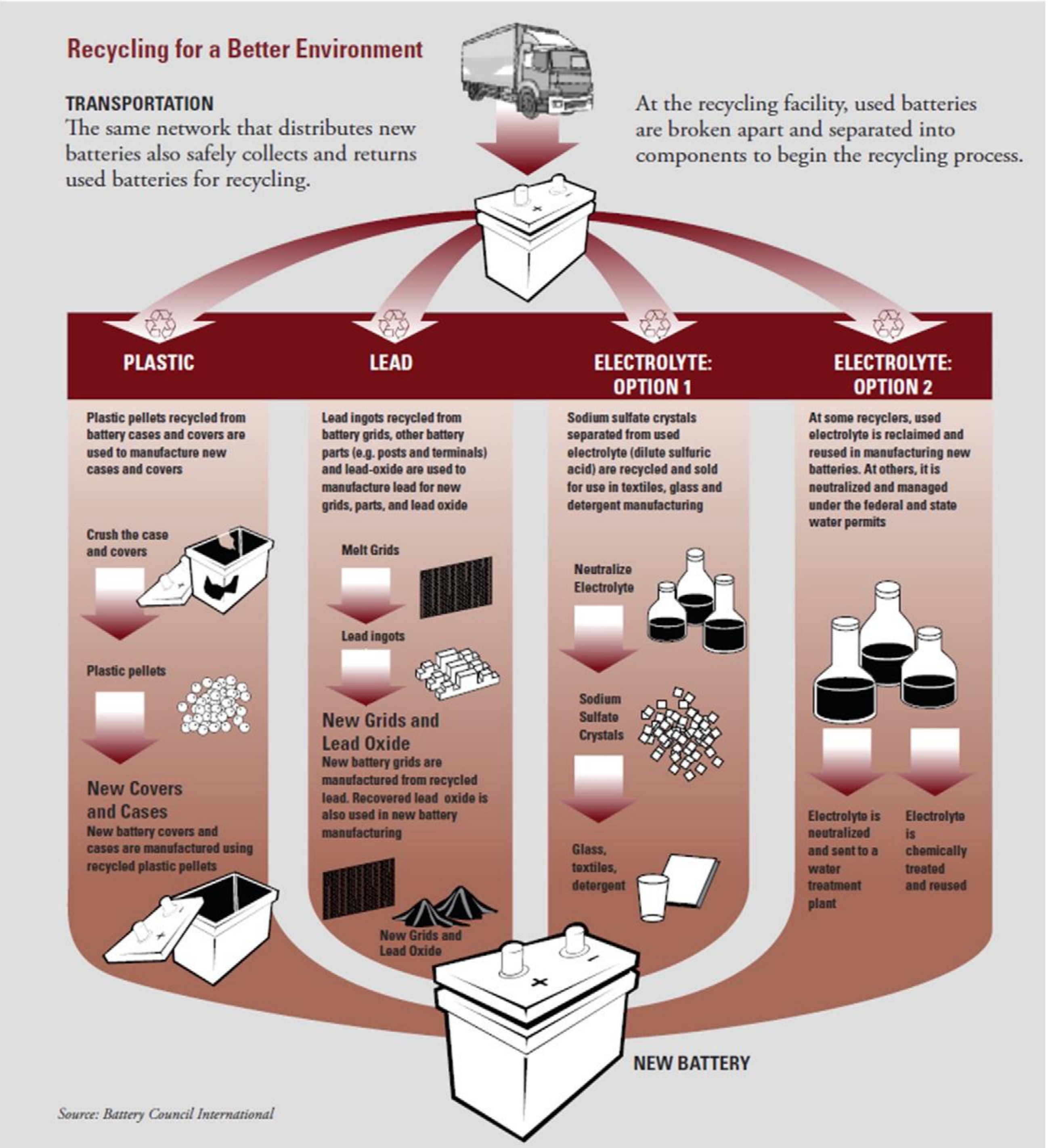
http://blog.lifespantechnology.com/it-asset-disposition-blog/bid/358505/What-are-the-issues-with-battery-recycling

Lead-Acid batteries are the most recycled consumer product.
(Courtesy of Battery Council International)



Sources:
Smith Bucklin Market Research and Statistics Group (2011 National Recycling Rate Study)
The Rubber Manufacturer's Association (2009 tire recycling rates) 10/2011
The American Forest & Paper Association (2010 paper recycling rates) 04/2012
The Aluminum Association (2010 aluminum recycling rates) 06/2011
Glass Packing Institute (2010 glass recycling rates) 04/2012
Environmental Protection Agency (2010 solid waste recycling rates) 12/2011

L. Gaines / Sustainable Materials and Technologies 1–2 (2014) 2–7 3



New Lead-Acid Battery Fees Beginning April 1, 2017

Effective April 1, 2017, the Act imposes a $1.00 California battery fee on the purchase of a replacement lead-acid battery and a $1.00 manufacturer battery fee on the sale of a lead-acid battery to a dealer, wholesaler, distributor or other person in California. On April 1, 2022, the California battery fee will increase to $2.00 and the manufacturer battery fee will no longer be due. The California State Board of Equalization (BOE) is responsible for the administration of these new fees in cooperation with the Department of Toxic Substances Control (DTSC).

Exide lead contamination

From Wikipedia, the free encyclopedia

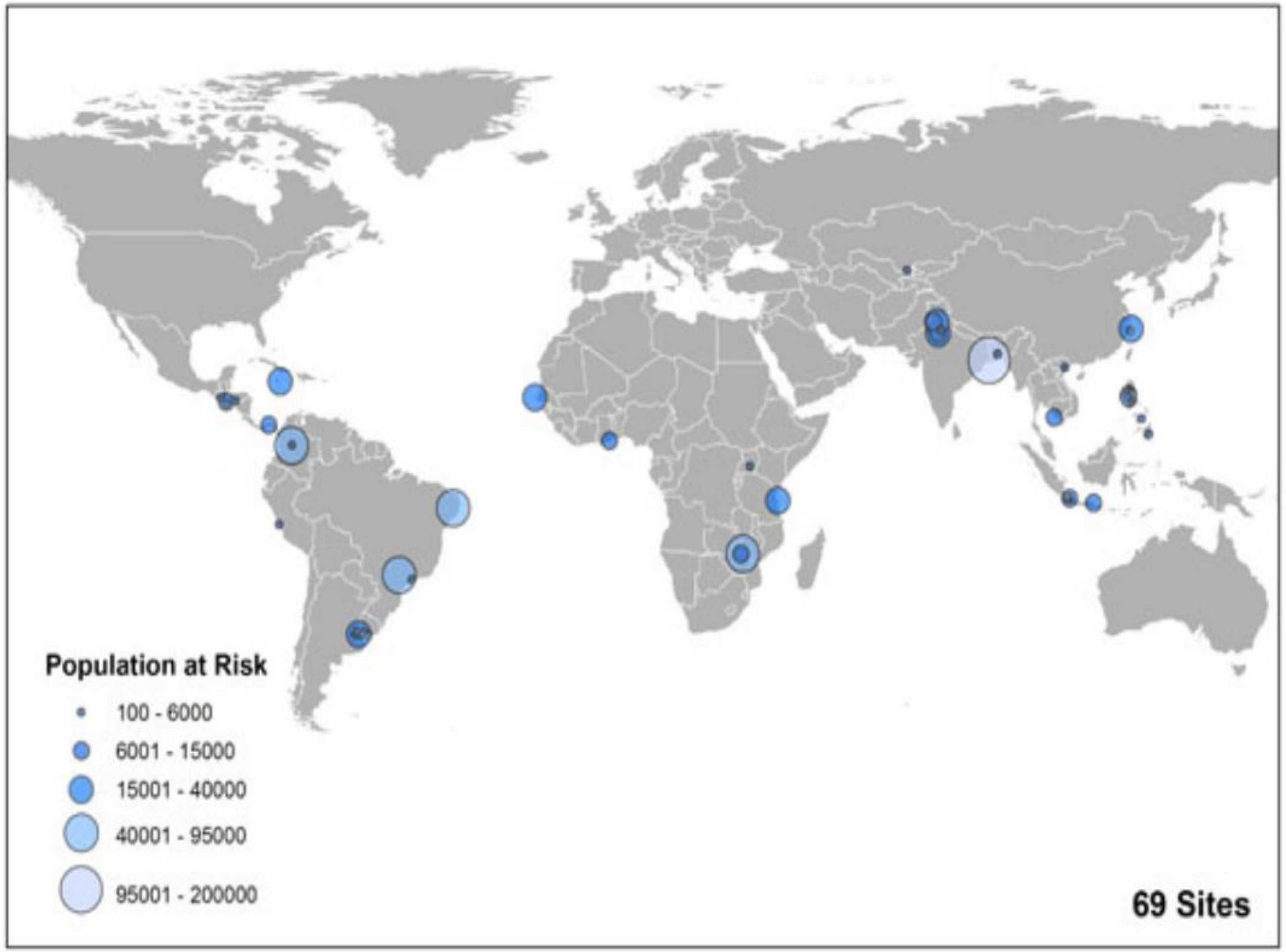
The **Exide lead contamination**, in southeast Los Angeles County, California, United States, came from a battery recycling plant that emitted lead, arsenic and other dangerous pollutants over decades that contaminated as many as 10,000 homes in half a dozen working-class, Latino communities near the plant. Exide Technologies, owner of the lead-acid battery smelter located in Vernon, agreed in 2015 to close the facility while the massive cleanup of the contaminated soil will take years and cost hundreds of millions of dollars.[1] The residents have

Lead-battery recycling has moved to Mexico

Originally published March 25, 2013 at 9:35 pm Updated March 25, 2013 at 11:46 pm

https://www.seattletimes.com/nation-world/lead-battery-recycling-has-moved-to-mexico/

Lead Pollution from Used Lead-Acid Battery Recycling



http://www.worstpolluted.org/projects_reports/display/90

What is Lead Poisoning?

- Is a medical condition caused by increased levels of heavy metal lead in the body
- Lead is known to be a cumulative toxicant
- Children and pregnant women are particularly vulnerable
- Major health risk and challenge in most developing countries and CEITs

Countries with Economies in Transition (CEITs)

Sources of Lead Poisoning in Developing Countries

- Lead mining and smelting
- Battery recycling
- Leaded gasoline
- Paint - Continuous use of lead in paint irrespective of safer alternatives known to be globally available.
- Traditional medicines
- Toys
- Discarded electronic devices

Above are also main source of global lead poisoning

4

"Issues of Lead Poisoning and Developing Countries", Babajide Alo (UNIVERSITY OF LAGOS, AKOKA, LAGOS, NIGERIA)

Composition/Value of Spent Lithium-Ion Batteries (LIBs)

Typical metal composition of spent mixed LIBs powder (wt.%).

Compound	wt.%
Co_2O_3	46.72
MnO	24.94
CuO	4.11
Li	2.67
P_2O_5	1.39
F	0.75
Al_2O_3	0.46
SO_3	0.27
Fe_2O_3	0.25
Cr_2O_3	0.25
CaO	0.22

Compound	wt.%
SiO_2	0.11
NiO	0.1
Na_2O	0.08
MgO	0.07
TiO_2	0.04
ZrO_2	0.01
Cl	0.01

A.A. Nayl, R.A. Elkhashab, Sayed M. Badawy, M.A. El-Khateeb, *Arabian Journal of Chemistry* (2017) 10, S3632–S3639

Table 1: LIB cathode compounds and their market values

Compound	Value (US$ per kg)	Citation
Cobalt	37.00	[13]
$LiCO_3$	6.40	[13]
$LiCoO_2$	18.30	[14]
$Li_3NiCoMnO_6$	10.80	[14]
$LiMnO_2$	3.70	[14]
$LiFePO_4$	1.50	[14]

A. Sonoca, J. Jeswiet, V. K. Soob, Procedia CIRP 29 (2015) 752 – 757

Recycling Process for Lithium-Ion: Smelter

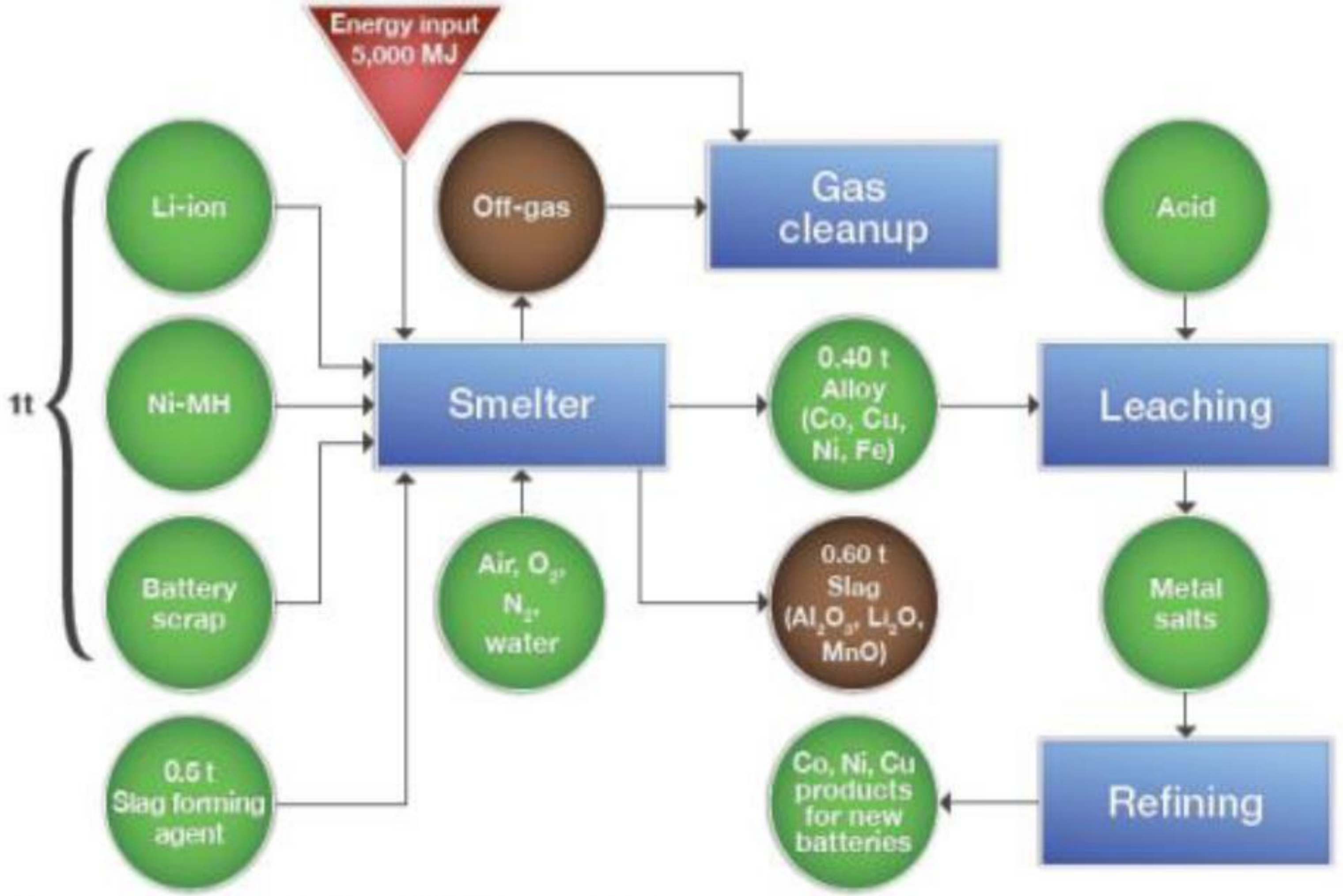


Fig. 1: Umicore process for 1 ton of lithium ion and Ni-Mh batteries

Co, Ni, and Cu recovered.
Li, Al, Mn go to slag which has some application as concrete additive.

A. Sonoca, J. Jeswiet, V. K. Soob, Procedia CIRP 29 (2015) 752 – 757

What’s next in lithium-ion for next 5 years?

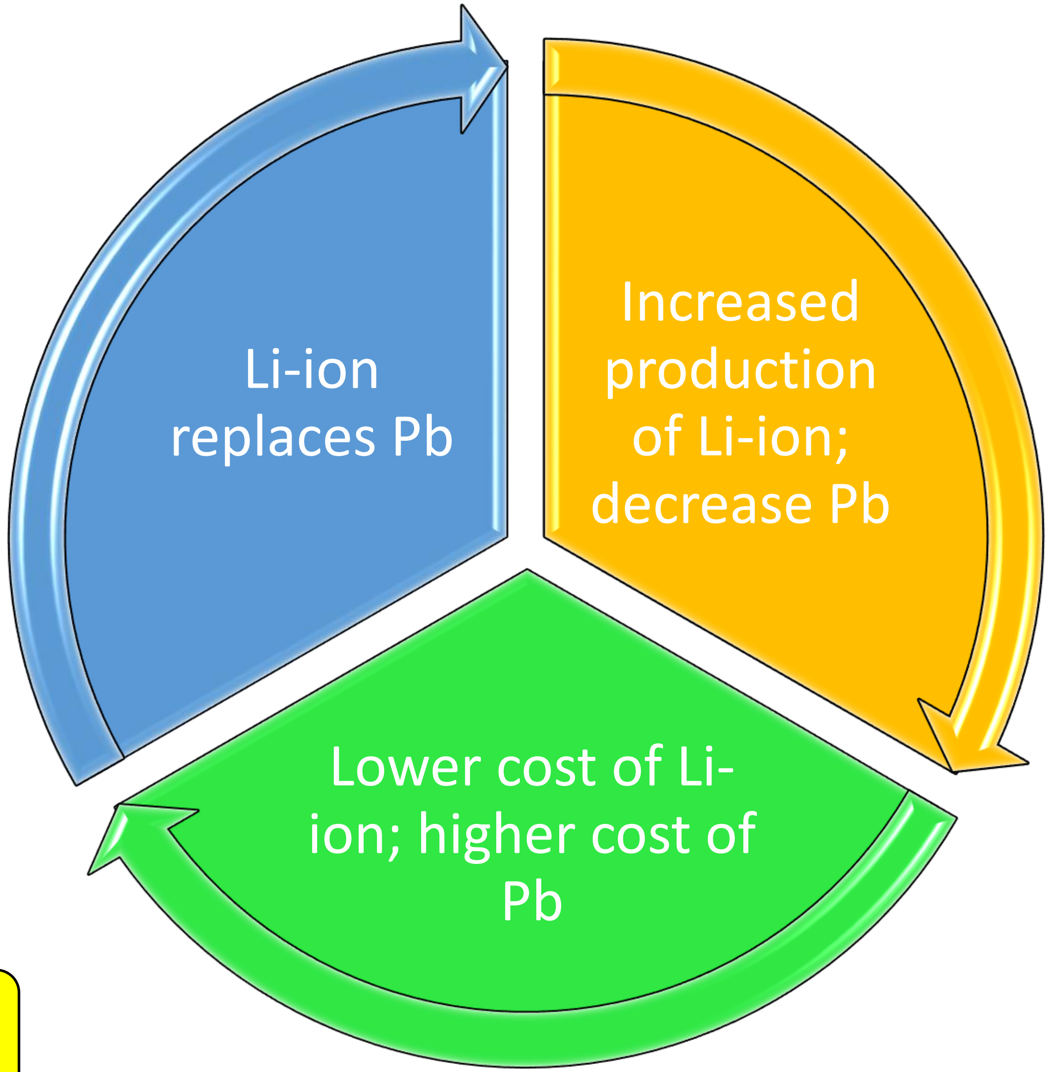
- Continued growth! Especially automotive and industrial markets.
- Improved Safety
  - Electrode coatings
  - More thermally stable separators
  - Composite electrolytes (Blend with solids to reduce solvent content)

- Higher energy cells
  - Higher voltage cells ($LiCoO_2$ > 4.4 V, NMC 811, 4.4 V)
  - Higher capacity cells (silicon blends with graphite)

Lithium-ion is well poised to be dominant battery chemistry

- Industrial applications such as UPS, forklifts, are switching to lithium ion
- Some cars eliminating lead acid (Hyundai Ioniq)
- Rechargeable lithium-ion replacing primary cells in some toys
- Li-ion share increasing in electric bike market in China

Over time, lithium-ion battery costs will decline while regulation may drive up costs of lead acid and primary cells.



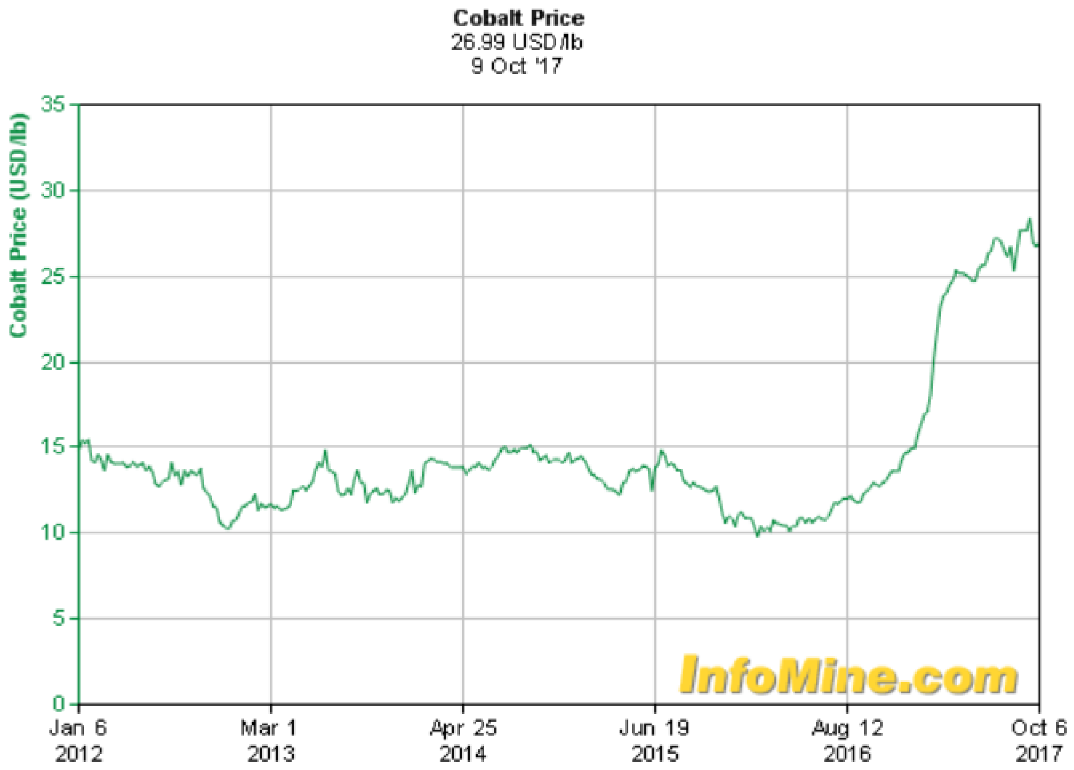
Impact of Li-ion recycling on costs?

Summary

- Major battery chemistries are alkaline (disposable), lead-acid and lithium-ion (rechargeable).
- Lithium-ion chemistries offers advantages over traditional alkaline and lead-acid chemistries in terms of performance but have cost and safety issues.
- Large scale production of lithium-ion is driving down costs; markets for lithium-ion continue to grow.
- Total cost of ownership analysis indicates advantage for lithium-ion over lead acid for some applications.
- Alkaline cells typically go to landfills, while lead-acid is mostly recycled. Regulations on lead recycling have driven many operations out of highly developed countries.
- Recycling of lithium-ion still immature; will recycling reduce lithium-ion cost even further?

Back-up

Lead Price
1.14 USD/lb
9 Oct '17
Lead Price (USD/lb)
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Jan 6 2012
Mar 1 2013
Apr 25 2014
Jun 19 2015
Aug 12 2016
Oct 6 2017
InfoMine.com

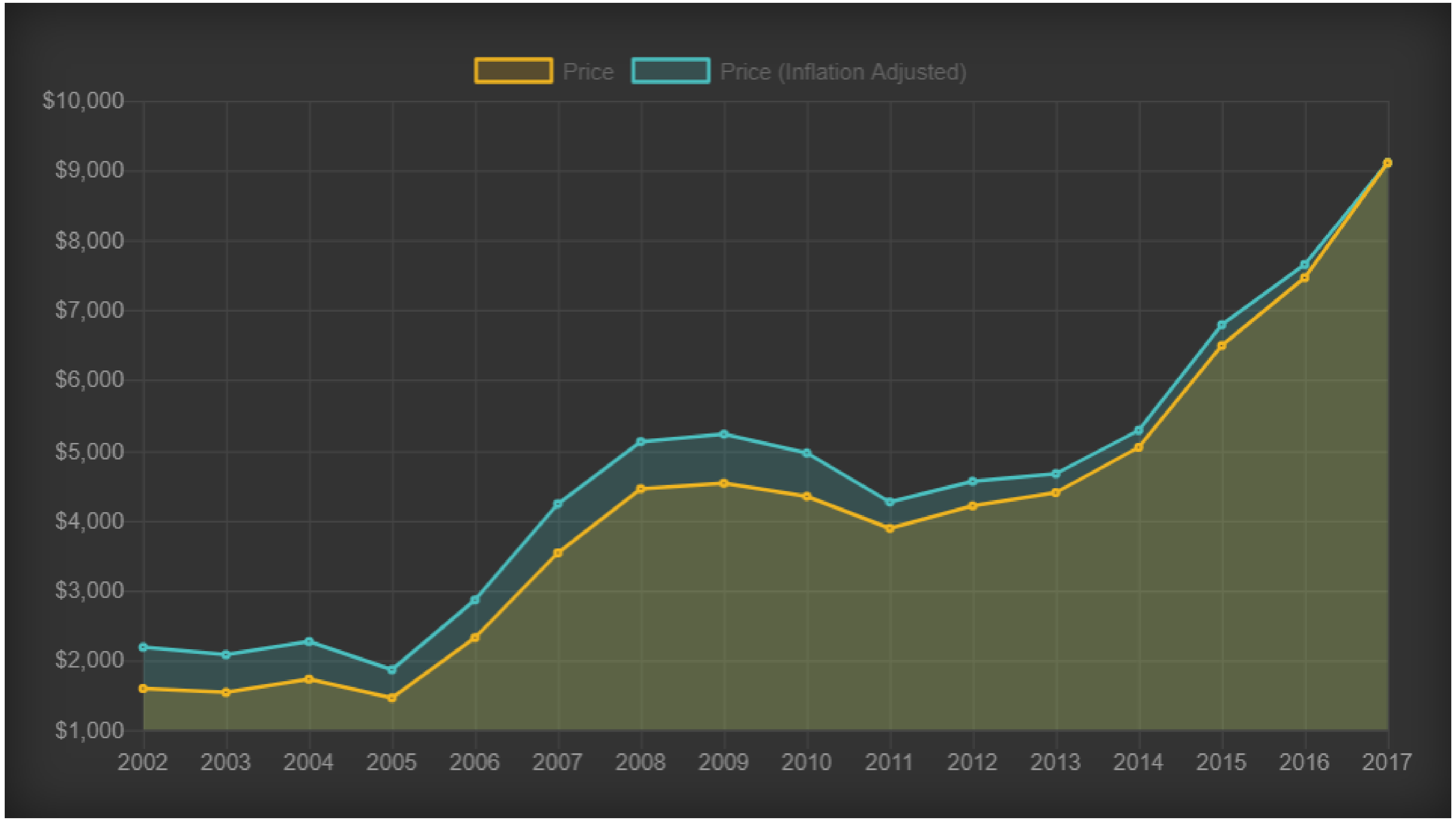


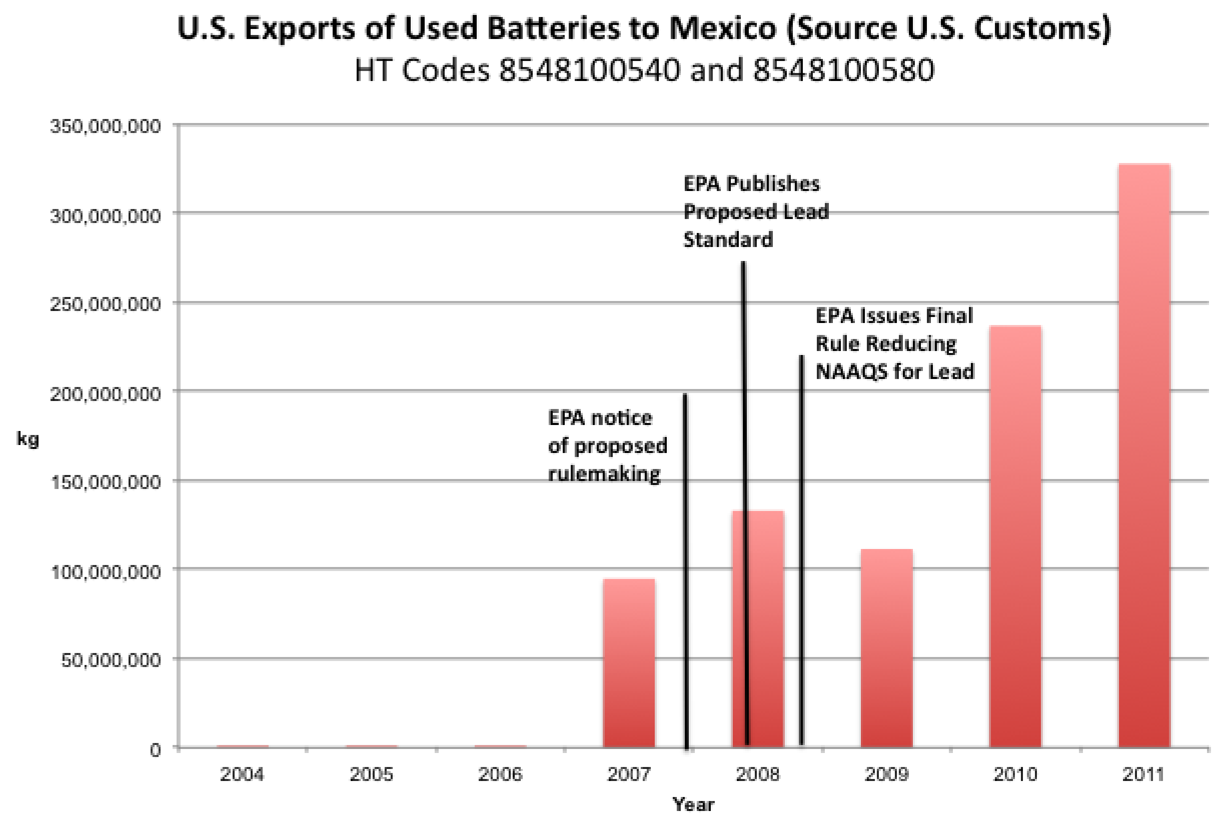
Cobalt Price
26.99 USD/lb
9 Oct '17
Cobalt Price (USD/lb)
35
30
25
20
15
10
5
0
Jan 6 2012
Mar 1 2013
Apr 25 2014
Jun 19 2015
Aug 12 2016
Oct 6 2017
InfoMine.com

Nickel Price
4.89 USD/lb
9 Oct '17
Nickel Price (USD/lb)
11
10
9
8
7
6
5
4
3
2
1
0
Jan 6 2012
Mar 1 2013
Apr 25 2014
Jun 19 2015
Aug 12 2016
Oct 6 2017
InfoMine.com

Zinc Price
1.51 USD/lb
9 Oct '17
Zinc Price (USD/lb)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Jan 6 2012
Mar 1 2013
Apr 25 2014
Jun 19 2015
Aug 12 2016
Oct 6 2017
InfoMine.com

Lithium price per metric ton





U.S. Exports of Used Batteries to Mexico (Source U.S. Customs)
HT Codes 8548100540 and 8548100580
350,000,000
300,000,000
250,000,000
200,000,000
150,000,000
100,000,000
50,000,000
0
kg
EPA notice of proposed rulemaking
EPA Publishes Proposed Lead Standard
EPA Issues Final Rule Reducing NAAQS for Lead
2004
2005
2006
2007
2008
2009
2010
2011
Year

Battery attribute	VRLA	Li-ion
Chemistry	Lead-acid	LMO/NMC
Rated power capacity	1 MW	1 MW
Runtime at 25°C (77°F)	6 minutes	6 minutes
Calendar life at 25°C (77°F)	5 years	17 years
Battery service life at 25°C (77°F)	4 years	12 years
Battery footprint	5.4 m^2 (59 ft^2)	2.2 m^2 (23 ft^2)
Battery weight	11,340 kg (25,000 lbs)	2,767 kg (6,100 lbs)
Fixed losses from trickle charging (as % of rated UPS capacity)	0.2%	0.1%
Battery materials cost	$0.06/W	$0.12/W
Battery management system cost	Incl. in battery cost	Incl. in battery cost

TCO	VRLA	Li-ion
Capital expense	$72,549	$132,366
Operational expense	$236,706	$55,762
TOTAL	$309,255	$188,128

Life Is On Schneider Electric

Battery Technology for
Data Centers: VRLA vs. Li-ion
by Victor Avelar
Martin Zacho
White Paper 229 (2016)